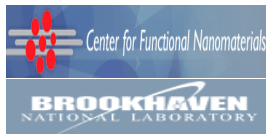


## 2D Atomically thin graphene nanoribbons – DNA self-assembled piezo structures for energy harvesting

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## Abstract

Graphene[1], widely known as single layered graphite, has generated lot of interests as generation next electronic material since its practical existence as free standing film. Its structural flexibility provides an opportunity to tune its electronic properties from being semimetal to semiconductor [2,3] for the fabrication of nanoscale devices[4]. Graphene nanoribbons (GNR) are defined as stretched graphene with straight edges and they transform from semiconductor to semimetal as the width of the ribbon changes and hence offer a variety of graphene. While there have been increasing interest in elucidating graphene nano-scale structures the development of a reproducible nanostructured assembly of graphene (nanoribbon) and DNA that could potentially lead to controllable and manipulative nano-scale mechanical devices have been very less explored. Recently Razdan, Patra and co-workers[5] have developed self assembled carbon nanotube-conducting polymer fibers. Also Sinha and members of his research group have a provisional patent and a pending patent application on a biosensor whose principle is based on the Carbon Nanotube (CNT)/DNA interaction. We will build on from the understanding on the previous work to establish a reproducible graphene-DNA nanostructured assembly that may consequently help develop graphene-DNA based bio-devices.

We plan to understand the attachment of graphene with single-stranded DNA by a self-assembly process under strong ultrasonication and in the resulting water-dispersible graphene-DNA hybrids. We intend to achieve monolayers of ss-DNA molecules adsorbed on both sides of the graphene sheets by a non-covalent – stacking and other secondary forces that will eventually lead to development of graphene-DNA based devices in the long run.

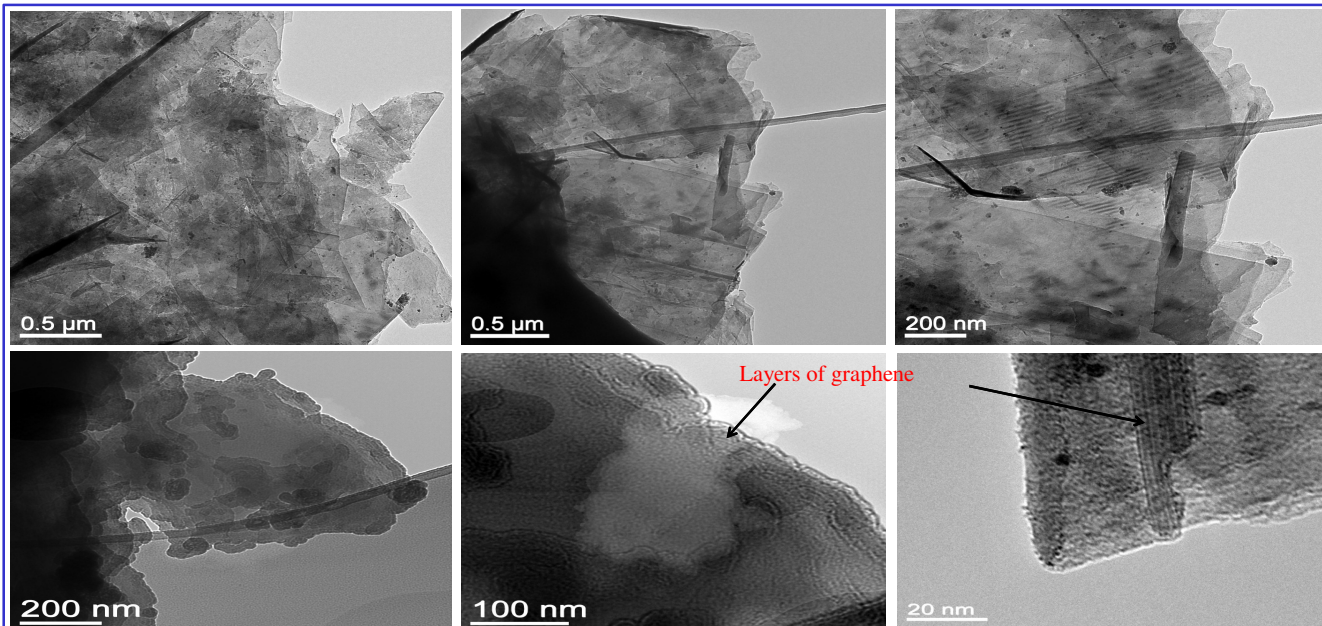


Figure 1. Structural and geometric morphology of 2-D Atomically thin graphene using TEM

## Experimental Procedure

Pyromellitic dianhydride-oxidianiline polyamic acid (PAA) in *N*-methyl-2-pyrrolidone (NMP) (15 wt %), NMP and *N,N'*-dimethylformamide (DMF) were used as the first of many polymers to make graphene-polymer composites. The PAA solution was diluted with NMP to 1 wt % prior to LbL assembly. GO was prepared from expanded graphite using the Staudenmaier procedure. Functionalized chemically converted graphene (f-CCG) was prepared using nitrobenzene diazonium salt treatment of surfactant wrapped CCG22 and reduced with elemental sulfur in the presence of NaHCO<sub>3</sub> (Scheme 1). A 0.1 wt % solution of f-CCG in DMF was used for the LbL assembly. Microscope slides (25mm × 75mm × 1 mm, Premiere) and silicon substrates were cleaned with piranha (30:70 v/v H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub>) solution and functionalized by 3-aminopropyl triethoxysilane (APTES) by immersing in a 1:9 (v/v) APTES:toluene solution for 1 h at 23 °C. After 1 h, the substrate was rinsed with freshly distilled toluene, sonicated in toluene for 10 min and rinsed with MeOH followed by drying with N<sub>2</sub> gas. PAA-f-CCG composite films were prepared by alternate dipping of the substrate into PAA and f-CCG solutions. The APTES functionalized microscope slide was immersed in a 1 wt % solution of PAA for 1 h. The slide was rinsed with copious amounts of NMP to remove the excess PAA followed by drying with N<sub>2</sub> followed by immersion in a 0.1 wt % f-CCG solution in DMF. And finally, the slide was rinsed with DMF (step d), followed by drying with N<sub>2</sub>. The deposition cycle resulting in a bilayer deposited on the substrate after each round (The LbL assembly was performed for 10 cycles). A schematic of the process is as shown in the Figure 2.

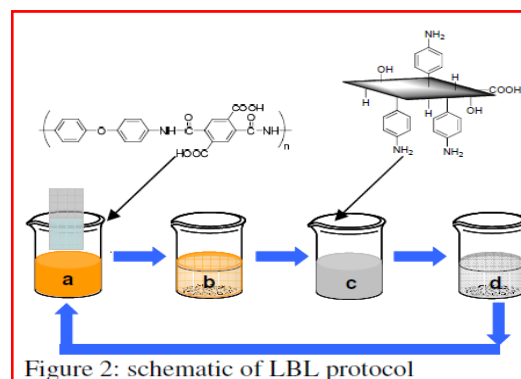


Figure 2: schematic of LBL protocol

## Future work

The first part of the graphene characterization has been demonstrated. The second part will focus on investigating possible applications of these structures. One would be to test the piezo-electric properties of coatings using DNA as the polymeric materials for the development of sustainable bio-piezo nanostructure in energy harvesting. The LbL assembled CCG-Polyimide as shown in figure 3 and CCG-DNA films may find potential application in fuel cell membranes, piezoelectric films and in electrodes for photovoltaics. Goal is to develop tailored CCG-DNA structures for piezoelectric energy harvesting and the fundamental understanding of structure-property-performance relationships of such hybrid materials.

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Figure 3: The structural color appearing in the graphene-polymer LBL films on deformation based reflection that can be converted to electrical signal (bio-piezo effect-Patra et al unpublished work)